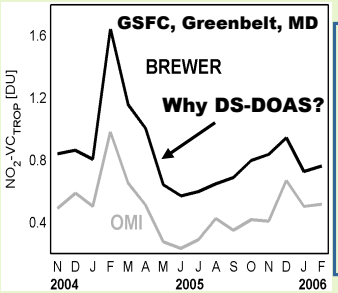

DS-DOAS: An Accurate Direct-Sun Method for Measuring NO_2 Total Column Content

Using a Brewer Monochromator and a Small Spectrometer

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Abstract: OMI and Sciamachy measurements have shown the global relationship between industrial activity and apparent amounts of NO_2 in the atmosphere. The method used to detect NO_2 from satellite observations is based on spectrally matching radiances obtained from measurements (400 to 465 nm) to those estimated from a radiative transfer calculation using laboratory absorption cross sections and an assumed NO_2 column content. Similar spectral fitting techniques, DOAS and MAX-DOAS have been applied to ground-based measurements of NO_2 and H_2O using scattered radiances. We use an alternate direct-sun technique, DS-DOAS, that has much higher accuracy than the scattered light measurements, does not depend on prior knowledge of the NO_2 or H_2O profile shape or assumptions of horizontal homogeneity, and has equivalent sensitivity to small NO_2 column content. The measurements are made using a newly developed portable system based on a small temperature stabilized commercial 1024 element CMOS spectrometer connected by fiber optic cable to a 1.5° collimator and filter wheel assembly. A precision pointing mechanism, 0.01°, is used to track the sun. The CMOS spectrometer simultaneously measures sun irradiances I(l) from 265 to 500 nm at 0.5 nm spectral resolution with ~3X oversampling. Direct-sun NO_2 and H_2O retrievals were obtained from measurements made in Thessaloniki, Greece during July 2006.

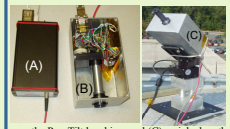

Figure 1: (A) The PAN-1 small 1024 element CMOS spectrometer with fiber optics coupling to (B) control electronics box, entrance optics, rotating filter wheel and shutter. (C) Field mounted fore optics and precision pan and tilt head with 0.01 degree pointing accuracy. The box shown mounted on the Pan-Tilt head in panel (C) weighs less than 1 kg. PAN-1 cost < $10K.

The PAN-1 system spectrometer is an **Avantes** Czerny-Turner optical design with a focal length of 75 mm, a diffraction grating covering a spectral range from l=270-520 nm with a spectral resolution of 0.5 nm, a slit of 50 microns, and a low noise 1024 **Hamamatsu** CMOS linear array that has almost no hot pixels. The spectrometer is connected to the sensor head by a 10 meter fiber optic cable, permitting the temperature sensitive spectrometer to be stored away from the sun in an off-the-shelf insulated thermoelectric cooler capable of maintaining the temperature within 2°C.

The Double Brewer Monochromator #171 was used to develop the NO_2 retrieval algorithm because of its well established wavelength and radiometric stability.

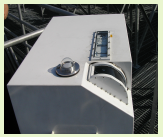

Figure 2 The modified Brewer with curved port and depolarizer.

Cede, Alexander, Jay Herman, Andreas Richter, Nickolay Krotkov and John Burrows, Measurements of Nitrogen Dioxide Total Column Amounts at Goddard Space Flight Center Using a Brewer Spectrometer in Direct Sun Mode, J. Of Geophys. Res., 111, D05304, doi:10.1029/2005JD006585, 2006

The NO_2 inversion method is described in detail [Cede et al., 2006], and is applied to the measured sun radiances between 335 to 365nm for the Brewer and 400 to 460 nm for PAN-1. Complete application of this method requires that the spectrometer has operated for a large number of days and is stable both radiometrically and in wavelength. Since PAN-1 is relatively new, none of these conditions have been established at this time. The self-calibration method applied to the Brewer spectrometer at GSFC (Bootstrap method) looked for a small subset of days when there was little or no NO_2 in the troposphere, and used these data to create a normalization against which high pollution days could be measured.

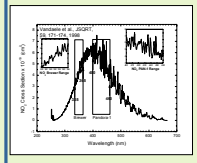

Figure 3: Laboratory NO_2 absorption cross sections

The results were corrected for a nominal stratospheric amount of ~0.1 DU, yielding a small residual bias of ~0.05 DU before instrumental and algorithm errors are considered. For the Brewer these are ±0.2 DU.

Since the Brewer spectrometer is known to be stable in both radiometric and wavelength calibration over long periods (more than 2 years), the bootstrap method works quite well within the above mentioned limitations and eliminates the need to independently know $I_0(l)$. In Thessaloniki, measurements of NO_2 were made every 3 minutes (PANDORA-1) and every 20 minutes (Brewer) over a two-week period.

A reference NO_2 value for PAN-1 was obtained by averaging the entire two-week's worth of Brewer NO_2 data and requiring that the corresponding average from PAN-1 matched the Brewer average. Therefore, the current accuracy, but not the precision, of the Thessaloniki PAN-1 NO_2 data is limited by the approximately ~0.2 DU error present in the Brewer data. However, the minute-to-minute precision is much higher (~0.01 DU) compared to the Brewer precision of ~0.4 DU. A future paper will discuss the long-term (multiple year) and laboratory calibrations, and operation of PAN-1 when the data are available.

Differences from the Brewer algorithm The most obvious differences are in the number of wavelengths used for PAN-1 (270) compared to the Brewer (6), the fact that PAN-1 measurements are simultaneous at all wavelengths, while the Brewer has a small time lag (~0.7 sec), PAN-1 is ~3x oversampled in wavelength, while the Brewer is undersampled. The Brewer operates between 340 and 360 nm and PAN-1 operates between 400 and 450 nm where the NO_2 structure is much larger (increased sensitivity to small changes in NO_2). PAN-1 obtained NO_2 measurements at least every 3 minutes compared to the Brewer cadence of 20 minutes. While in Thessaloniki using PAN-1, we did not have an absolute radiometric calibration. This required that we use the Brewer NO_2 and CIMEL H_2O 2-week average to obtain an effective radiometric normalization for the 400 to 460 nm range. Each PAN-1 spectrum is the average of 50 to 2500 measurements in 20 seconds depending on exposure time (8 to 400 ms, full sun to clouds). This reduces the noise for clear-sky measurements compared to the Brewer.

The first steps of the algorithm are nearly identical, namely, using simple radiative transfer Beer's law calculations: 1) removal of the Rayleigh scattered component obtained by knowing the surface pressure and using a standard atmosphere, 2) removal of the aerosol scattered component by simultaneously solving for the optical depth as a function of wavelength l (Figure 4 Panel C) and Angstrom coefficient a, 3) removal of residual O_3 absorption between 400 and 460 nm using ozone amounts obtained directly from Brewer measurements at 305 to 320 nm, and removal of the O_2:O_2 absorption in the vicinity of 340 and 360 nm for the Brewer and in the vicinity of 441 nm for PAN-1. Since both the Brewer and PAN-1 made direct-sun measurements, multiple scattering and Ring effect corrections are not necessary, and estimations of the air-mass factor is a simple geometric cosine correction.

Next, the optical depths of NO_2 as a function of wavelength are computed using the laboratory absorption cross sections (Figure 3) and assuming different amounts of NO_2 in the atmosphere from 0.1 to 3DU (1 DU = 2.69×10^{16} molecules/cm^2). After processing the entire two weeks of data, we require that the average NO_2 from the Brewer match the average NO_2 from PAN-1. We force the averages to match by applying a wavelength-independent factor to the measured I(l) counts. The effect is a normalization of the PAN-1 measured radiances based on a single number obtained from the Brewer spectrometer. Since the Brewer obtained normalization is the average of approximately 100 independent measurements, the random errors are largely removed, leaving only a small residual bias that was previously discussed.

The measured NO_2 optical depths are now computed and the results are compared with the calculated model optical depths as shown in Figure 4A. Finally, the amount of H_2O is estimated by using an irradiance normalization obtained from the 10-day average of CIMEL measured water amounts and the laboratory H_2O absorption coefficients for the band in the vicinity of 441 - 450 nm. The results of this procedure are shown in Figure 4B and are subtracted from the NO_2 data. Panel A shows the computed optical depth (blue) for 0.54±0.01 DU of NO_2 compared to the optical depth (red) estimated from the measured solar irradiances for 21 July 2006 at 14:39:55. The PAN-1 NO_2 uncertainty is estimated from the 3% (1 standard deviation) in the NO_2 residuals in panel D. At the same time, the Brewer spectrometer measured 0.69±0.5 DU. Panel B shows the amount of water vapor in the atmosphere to be 2.5 cm compared to the simultaneously measured CIMEL value of 2.91 cm at 940±5 nm. Panel C shows the measured aerosol optical depth fitted as a function of wavelength fitted by a quadratic smoothing function. Panel D shows the residuals in optical depth formed by taking the difference between the values obtained from the measured radiances and those calculated from the laboratory absorption cross sections in Panel A.

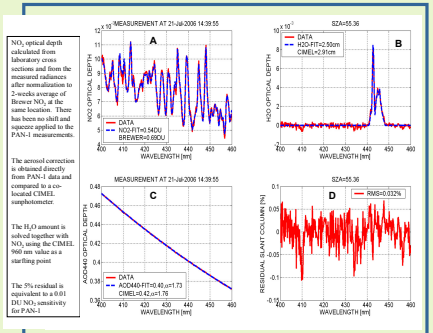

Figure 4 Sample solution for NO_2 and H_2O at Thessaloniki for 21 July 2006 at 14:39:55

Field Measurements: Measurements of direct-sun irradiances were made at the city of Thessaloniki, in Greece (latitude 40.5° North, longitude 22.9° East). The instruments were set up on an elevated platform on top of the Aristotle University Physics building, about 60 meters above sea level, as part of the July 2006 Greek-EU Scout-O3 campaign. After instrument setup, a Brewer, PAN-1, UV-MFRSR, and a CIMEL made measurements throughout the day from 13 July to 23 July under all sky conditions. All four instruments measured 2 out of 3 aerosol parameters (optical depth, Angstrom coefficient, and absorption coefficient) in different ways, the Brewer and PAN-1 measured NO_2, PAN-1 and the CIMEL measured H_2O, and the Brewer and the UV-MFRSR measured O_3. PAN-1 also measured O_3, but these data have not yet been processed as they require a laboratory calibration of the UV bandpass filter.

Results: The measurements of interest are those mainly related to NO_2, with the measurements of other gases and aerosols serving as auxiliary data. The auxiliary data permits us to remove Rayleigh scattering, aerosol effects, and ozone absorption, leaving the NO_2 residual in the data as described in Cede et al. [2006]. A typical set of measurements is shown for 17 July 2006 in Figure 5, where we show the daily courses of column NO_2 (panel A), H_2O (panel B), aerosol optical depths AOD (panel C), and the aerosol Angstrom coefficient a (panel D). The Angstrom coefficient a is a measure of particle size, smaller values indicating larger particles.

For most of the day, the measured values of the PAN-1 AOD and a track those measured by the CIMEL sunphotometer at the same wavelength (440 nm). In addition, we show the same parameters measured by the Brewer at 363 nm. There are periods where the PAN-1 values are quite different than those from the CIMEL caused by a sun-tracking algorithm error that did not track the center of the sun. This results in a small apparent intensity reduction that is indistinguishable from having additional aerosol in the atmosphere. The error is particularly apparent in a, which has greater sensitivity to pointing errors than AOD. The small pointing error does not affect the spectral fitting technique for NO_2 and H_2O, since these are fits to relative values at different wavelengths that does not change the peak to trough ratios for a given amount of NO_2 or H_2O in the atmosphere (see figure 4).

On 17 July 2006, the daily course of NO_2 is shown in Figure 5A for both the Brewer and PAN-1. Because the Brewer uses only six non-simultaneous wavelengths, operates in a reduced sensitivity region, and has less averaging, the Brewer data have much greater uncertainty (blue dots and error bars) than PAN-1 (red dots). The PAN-1 precision is about ±0.01 DU, which is about the width of the red dots shown in Figure 5A. The clear-sky portion of the daily course seen by the Brewer and PAN-1 agree with each other within the Brewer error bars. Once PAN-1 operates long enough to be self-calibrated, or is accurately laboratory calibrated, the intrinsically higher precision of PAN-1 should make its NO_2 values the reference for intercomparisons with Brewers and other passive instrumentation.

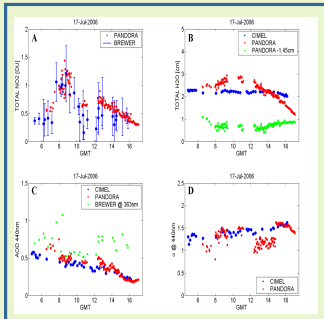

Figure 5 A comparison between 3 different instruments (PAN-1, Brewer, and CIMEL) for the daily variation of aerosol parameters and NO_2 column content. Panel A shows column NO_2, panel B shows column H2O, panel C shows the aerosol optical depth (AOD), and panel D shows the Angstrom coefficient a.

Because of an error in the azimuth pointing control calculation, there is an occasional error that affects the AOD and a, but not NO_2 or H_2O that rely on ratios. Most of the time Pan-1 agrees with the CIMEL AOD and a at 440 nm. On some days, the H_2O column amount had to be reduced substantially below the CIMEL value to remove an apparent air mass effect in PAN-1. The origin of this problem might be in a possible temperature dependence of the absorption cross sections that were not used in the current algorithm.

NO_2 Daily Data The daily NO_2 data for the period 14 July to 24 July 2006 are shown (Figure 6) for both the Brewer (20 minutes) and for PAN-1 (3 minutes). Some of the days when the data were obtained were partly cloudy, with the sun going in and out of clouds. Thin clouds do not affect the PAN-1 data, since the wavelengths are obtained simultaneously. The same is not true for the Brewer, where the 6 wavelengths are obtained sequentially over a short interval with each wavelength integrated for 0.1147 seconds, or about 0.7 seconds for all six wavelengths. This is sufficient time for the radiances to change because of changes in cloud and aerosol transmission. The result is additional scatter in the Brewer estimates of NO_2 as is clearly shown in Figure 6. This effect is particularly seen on Saturday 15 July where the PAN-1 data are highly correlated from measurement to measurement, while the Brewer data show substantial random scatter that is greater than their estimated error.

On Sunday, 16 July, there was fairly heavy cloud cover. This is clearly seen in the scatter of the PAN-1 data (red dots), which persisted into Monday morning, 17 July, after which the data are again highly correlated. There is missing data on the 18th and 19th where PAN-1 was not working. There also was almost no Brewer data on the 18th.

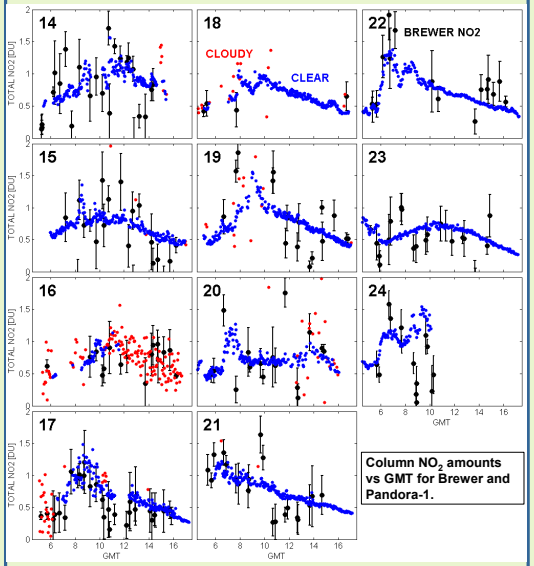

Figure 6 NO_2 daily course for Friday 14 July to Monday 24 July 2006 at Thessaloniki, Greece. The blue dots represent PAN-1 data and black dots and error bars are from the Brewer spectrometer. The precision of the PAN-1 NO_2 values is 0.01 DU.

Note that PAN-1 can measure NO_2 even in the presence of light clouds with just slightly increased scatter, and heavier clouds with more scatter (see 16 July). The Brewer data is cloud screened, since the six wavelength measurements are not simultaneous (~0.7 sec).